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EXTRACTION PROPERTIES OF

4-TETRA(HYDROXYPHENYL)-BTPHEN IN LIQUID-LIQUID

EXTRACTION SYSTEMS WITH CYCLOHEXANONE/OCTANOL OR IN A SOLID-PHASE EXTRACTION SYSTEM

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Dedicated to Professor Kaoru Fuji on the occasion of his 80th birthday

Abstract – The extraction properties of tetra(4-hydroxyphenyl)-BTPhen have been investigated. Liquid-liquid extraction studies in proposed SANEX diluents, cyclohexanone and 1-octanol, indicate that actinide-lanthanide separation is superior in cyclohexanone; whereas actinide-actinide separation is more efficient in 1-octanol. Immobilization of the ligand onto a silica support results in the separation factor becoming dependent upon the concentration of nitrate anions in the aqueous phase. The immobilized ligand was also applied to the extraction of transition metals, resulting in >70% uptake of all transition metals examined, in the presence of alkali and alkaline earth metals.

INTRODUCTION

Spent nuclear fuel (SNF) consists largely of uranium (U, 94%), fission and corrosion products (Sr, Cs, I, Tc, Ni, Pd, Ag, Cd 4-5%) plutonium (Pu, 1%) and minor actinides (Np, Am, Cm, 0.1%). The fission products are responsible for the majority of the radiotoxicity of SNF; however, their short half-lives result in a quick decrease in radiotoxicity. On the other hand, the major long-term radiotoxicity is caused by the minor actinides (Np, Am and Cm), despite contributing only 0.1% to the spent fuel mass.¹⁻³ After removal of U and Pu by the plutonium-uranium reductive extraction process (PUREX), the separation of actinides from fission products, particularly the chemically very similar lanthanides, is crucial to allow partitioning and transmutation of the actinides to reduce the radiotoxicity of the waste further.⁴ The transmutation process

may be carried out in new Generation IV reactors or ADS (Accelerator Driven Systems) dedicated transmuters where high-energy neutrons are used to convert the actinides into shorter-lived radionuclides or stable elements. In such reactors, the high neutron-capture cross-section of the lanthanides would be a hindrance to the transmutation process.

RESULTS AND DISCUSSION

The selective actinide extraction (SANEX) process currently involves a liquid-liquid extraction process using hydrophobic ligands containing multiple soft *N*-donor atoms to separate actinides from lanthanides selectively.^{5–7} The SANEX process is typically carried out with an aqueous phase containing nitric acid with a ligand dissolved in the organic phase.⁸ 6,6'-Bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo[1,2,4]triazin-3-yl)-2,2'-bipyridine (CyMe₄-BTBP) **1** (Figure 1) is the current European benchmark ligand for the SANEX process. It is capable of performing selective actinide extraction, and a laboratory demonstration has been successfully carried out on post-PUREX raffinate.⁹ Quadridentate ligands such as CyMe₄-BTBP **1** exploit the more covalent nature of the metal-ligand bond with actinides, as a result of more diffuse nature of the actinide 5*f* orbitals that extend further than the 6*d* orbitals.¹⁰ The more recently developed CyMe₄-BTPhen **2** (Figure 1) has improved An/Ln separation performance, at least in part due to being locked into the binding conformation.^{11–13} In 1-octanol, CyMe₄-BTPhen **2** has an extraction efficiency of 2 orders of magnitude higher than CyMe₄-BTBP **1** along with faster extraction kinetics.^{13,14} Different analogues of the BTPhen system have been tested to determine the most effective structure for actinide separation. This paper investigates the extraction efficiency of tetra(4-hydroxyphenyl)-BTPhen **3** (Figure 1) in cyclohexanone and octanol at various nitric acid concentrations. Ligand **3** was also immobilized onto functionalized silica via the phenolic groups and we report herein the effect of nitrate ions concentration upon An/Ln separation factor, as well as the uptake of possible fission products.

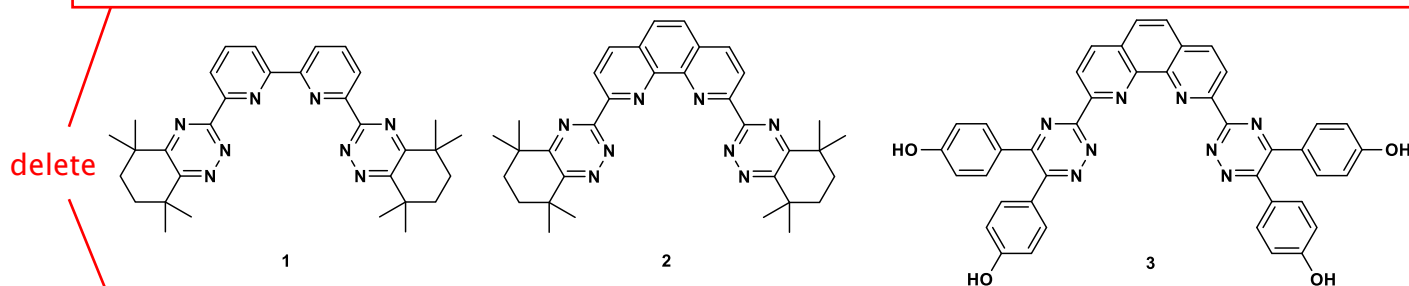


Figure 1: Structures of CyMe₄-BTPhen **1**, CyMe₄-BTBP **2** and tetra(4-hydroxyphenyl)-BTPhen **3**.

Prospective diluents for the SANEX process must display high organic solubility of the ligand and its complexed species, high flashpoint, low water solubility (to avoid formation of emulsions), high stability in acidic media (4 M HNO₃), resistance to radiolysis and be available in industrial quantities at low cost.^{16,17}

Both cyclohexanone and 1-octanol fulfil these requirements and have been proposed to be used in model SANEX processes. Tetra(4-hydroxyphenyl)-BTPhen **3** is more soluble in cyclohexanone (higher than 10 mM) than in octanol (5 mM), which raises the possibility for better extraction efficiency. However, 1-octanol is less water-soluble and has been used in other actinide separation processes around the world.^{18,19} Therefore, the comparison between different diluents is crucial to find the optimum solvent for any SANEX process.

An alternative to a liquid-liquid separation is the use of a liquid-solid process where the immobilization of actinide-selective ligands onto a solid support averts the need for phase separation and mixing; removing the requirement for large volumes of solvent that results in the concomitant generation of large amounts of waste.^{18,19} This technique is particularly advantageous for the recovery of small quantities of metals from bulk solution.²² In general, such separation materials can be classified as extraction chromatographic (EXC) resins or solid-phase extractants (SPE) depending on their nature. Extraction chromatographic resins typically comprise a ligand that is impregnated into an inert support. The behavior of such materials can be readily described / predicted using the properties of the ligand in liquid-liquid extraction. Contrary to EXC, solid-phase extractants represent solid supports that have been derivatized by selective ligands that are covalently bound to the support.²³ Extraction chromatographic separation studies of the trivalent actinides and lanthanides have been demonstrated using various *N*-donor ligands (BTP, BTBP and BTPhen derivatives) on different supports (SiO₂-P, PAN, XAD resin).²⁴⁻³² A recent example of solid-phase extractants developed for actinide–lanthanide separation include the triazine soft *N*-donor (Me₄BTPhen) linked covalently with poly(vinylbenzyl) chloride to generate PVB–Me₄BTPhen.³³ In an earlier study, we have demonstrated that tetra(4-hydroxyphenyl)-BTPhen functionalized silica gel **4** (Figure 2) was able to extract actinides from lanthanides with a separation factor $SF_{Am/Eu} \approx 140$ in 4 M HNO₃.³²

Much of the focus of fuel reprocessing has been on the separation of actinides from lanthanides and far less has been on the partitioning of adjacent minor actinide elements Am(III) and Cm(III) and no such large-scale process is currently available. Cm(III) produces a lot of heat in the decay process and cannot be transmuted with Am(III) as the excess heat will cause problems in fuel fabrication, requiring additional shielding.³⁴ The separation of Am(III) and Cm(III) is challenging due to their similar ionic radii and bond forming properties and is possibly one of the most difficult separations in the overall partitioning and transmutation process.^{35,36} Many different approaches have been studied including high-pressure ion exchange, extraction chromatography and solvent extraction using di(2-ethylhexyl)phosphoric acid (HDEHP). More recently, we've shown separation of Am(III) and Cm(III) ($SF_{Am/Cm} = 7.9$).^{21,37-39}

delete The same shall apply hereinafter.

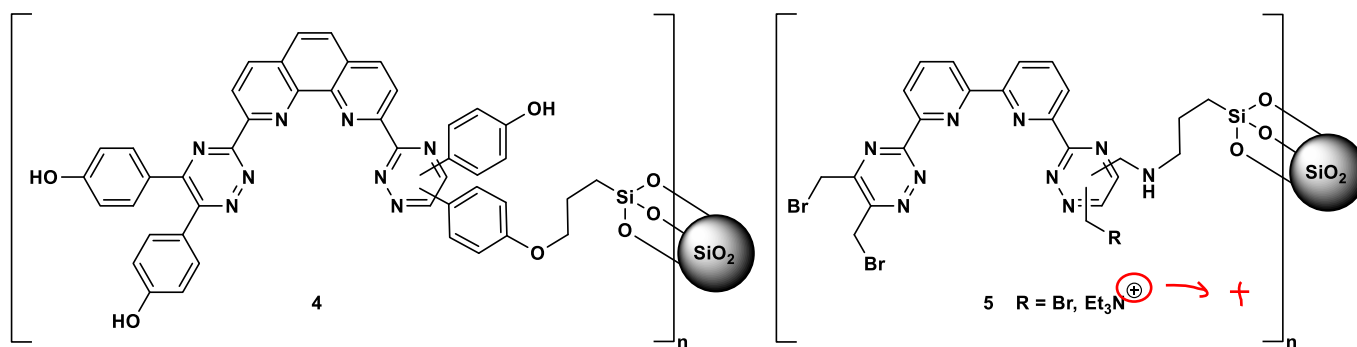


Figure 2. Structure of tetra(4-hydroxyphenyl)-BTPhen functionalized silica gel **4** and tetra-bromomethyl-BTBP on functionalized silica gel **5**.

Separation of the minor actinides from the corrosion and fission products such as Ni, Pd, Ag and Cd is crucial to simplify the separation of the trivalent actinides destined for transmutation.⁴⁰ CyMe₄-BTBP co-extracts the fission products with the minor actinides, but is a poor extractant of U and Pu, hence our previous publication proposed the use of a two column technique, one for extracting fission and corrosion products, and another for extracting the minor actinides. This technique requires the fabrication and use of two different types of ligand, complicating the process. Production of similar ligands with mostly identical reagents and synthesis steps that produce the ligands that meet the differing specifications would therefore be advantageous.

The distribution ratios D_{Am} and D_{Eu} and separation factors ($SF_{Am/Eu}$) shown in Figure 3 and Figure 4 display the separation for Am(III) over Eu(III) for the tetra(4-hydroxyphenyl)-BTPhen ligand **3** in cyclohexanone and in octanol respectively, as a function of nitric acid concentration (0.001 – 4 M). The value of the separation factor close to unity in 0.001 M HNO₃ in cyclohexanone (Figure 3) indicates that, in this diluent, the ligand **3** does not distinguish Am(III) over Eu(III) at low concentrations of nitric acid. However, the overall trend in the separation factors for cyclohexanone shows an increase in separation factor with increasing concentration of nitric acid, with separation factors at 0.5 M and 1 M HNO₃ ($SF_{Am/Eu} = 26.0 \pm 1.5$ for 1 M HNO₃) suggesting either pH or the ligating effect of nitrate ions is affecting the selectivity. Unfortunately, the distribution ratios for Am(III) (D_{Am}) were rather low, with the highest value being observed in 1 M HNO₃ with $D_{Am} = 1.7 \pm 0.1$. These data imply that in cyclohexanone **3** can differentiate Am(III) over Eu(III) at > 0.5 M HNO₃ but its extraction efficiency is too low.

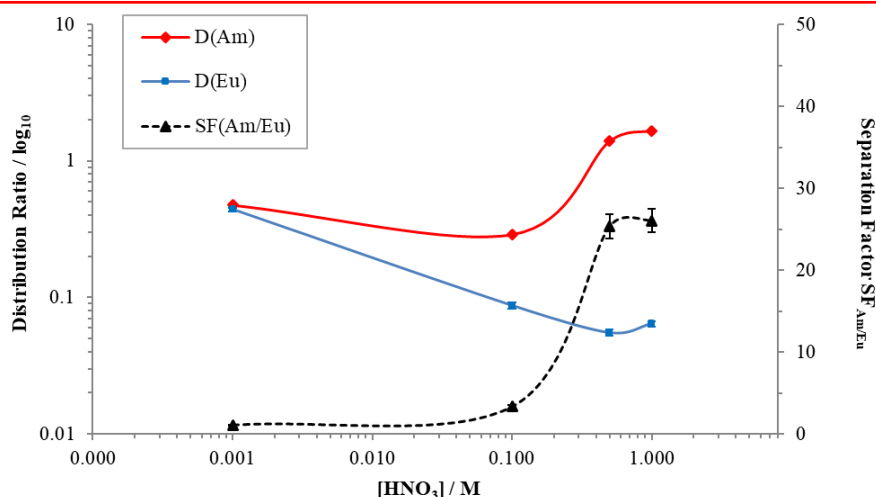


Figure 3 Extraction of Am(III) and Eu(III) by 10 mM tetra(4-hydroxyphenyl)-BTPhen 3 in cyclohexanone as a function of nitric acid concentration. The system was shaken for 90 mins at 1800 rpm.

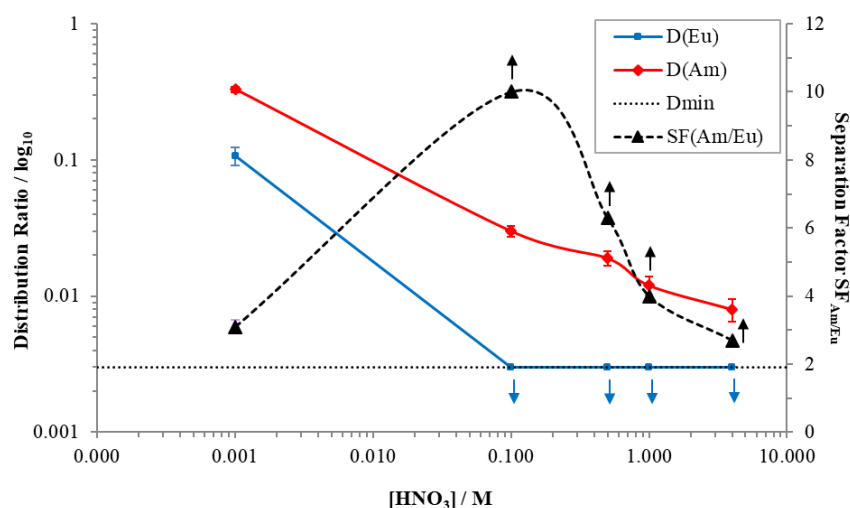
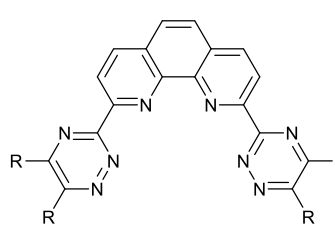
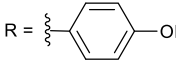

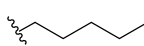
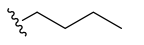



Figure 4 Extraction of Am(III) and Eu(III) by 5 mM tetra(4-hydroxyphenyl)-BTPhen 3 in octanol as a function of nitric acid concentration. The system was shaken for 90 mins at 1800 rpm.

With octanol as diluent (Figure 4), the most surprising finding is the decreasing trend of D_{Am} with increasing nitric acid concentration. This is in contradiction to the behaviour of all the BTPhen- and BTBP-family ligands studied previously in octanol and may be due to hydrogen bonding interactions between the relatively acidic phenolic groups on the ligand and the octanol solvent. The D_{Am} distribution ratios observed in octanol were even lower than those in cyclohexanone and did not exceed unity under any conditions.

The data indicates that octanol is not an efficient diluent for actinide extraction from lanthanides for ligand **3**.

Table 1 Comparison of distribution weight ratios and separation factors of similar BTPhen ligands in 1-octanol

<div style="display: flex; justify-content: space-around; align-items: center;">  <div style="display: flex; flex-direction: column; align-items: center;"> <div>R =  3</div> <div>R =  2</div> </div> <div style="display: flex; flex-direction: column; align-items: center;"> <div>R =  6</div> <div>R =  7</div> </div> <div style="display: flex; flex-direction: column; align-items: center;"> <div>R =  8</div> </div> </div>			
Entry	Name	$D_{w,Am}$ at 4M HNO ₃	SF _{Am/Eu} at 4M HNO ₃
1	to small betti. Tetra(4-hydroxyphenyl)-BTPhen 3	0.008 ± 0.001	>2.7
2	CyMe ₄ -BTPhen 2	1314 ⁴¹	398
3	C5-BTPhen 6	101 ⁴²	178
4	n-C4-BTPhen 7	ca. 50 ⁴³	ca. 125
5	to small betti. Sec-C4-BTPhen 8	ca. 100 ⁴³	ca. 210

Surprisingly, unlike other BTPhen ligands **2**, **6**, **7**, **8**, ligand **3** shows very low $D_{w,Am}$ and separation factors (Table 1). This phenomenon may be a result of mesomeric electron donation by the phenolic groups increasing the pK_a of the triazole rings.

Figure 5 shows the distribution ratios of Am(III) and Cm(III) (D_{Am} and D_{Cm}) for tetra(4-hydroxyphenyl)-BTPhen **3** in cyclohexanone and the corresponding separation factors. In addition to the $D_{Am-gamma}$ (similar to the case of D_{Eu} measurement), D_{Am} values measured by alpha-spectrometry are shown in the graph. Excellent agreement of the $D_{Am-gamma}$ with the D_{Am} values serves as validation of the experimental procedure. Whilst there is an increasing separation factor as the concentration of nitric acid increases, the maximum value ($SF_{Am/Cm} = 2.1 \pm 0.2$ at 1 M HNO₃) is below the values observed previously for other ligands in this family. As discussed above, the Am(III) distribution ratios are rather low and D_{Am} exceed unity for $[HNO_3] \geq 0.5$ M ($D_{Am} = 1.6 \pm 0.1$ for 1 M HNO₃). The distribution ratios show that, in cyclohexanone, this ligand is show moderate selectivity for Am(III) over Cm(III) at higher concentrations of nitric acid.

The octanol studies of **3**, shown in Figure 6, indicate rather scattered separation factors. At higher concentrations of HNO_3 ($[\text{HNO}_3] \geq 0.5 \text{ mol/L}$), both the D_{Am} and D_{Cm} are close to, or even below, the limit of detection. Hence, this system is not a candidate for Am (III) / Cm (III) separation.

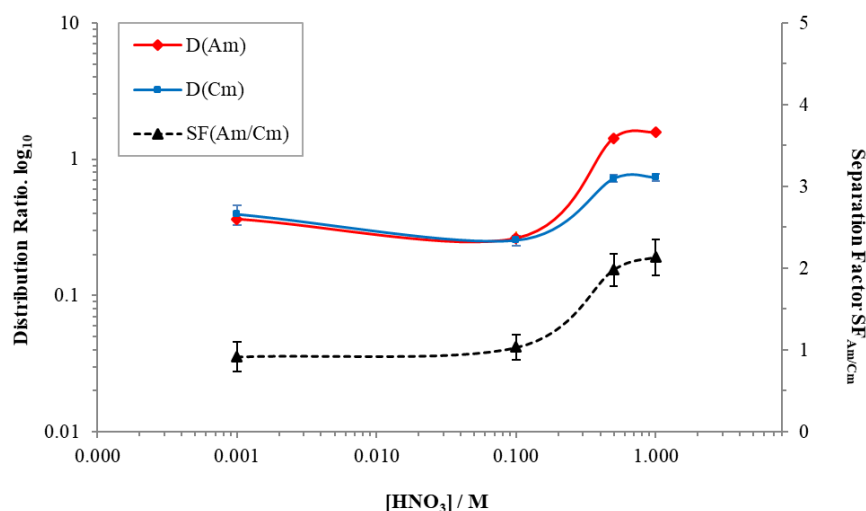


Figure 5 Extraction of Am(III) and Cm(III) by 10 mM tetra(4-hydroxyphenyl)-4BTPhen **3** in cyclohexanone as a function of nitric acid concentration. The system was shaken for 90 mins at 1800 rpm.

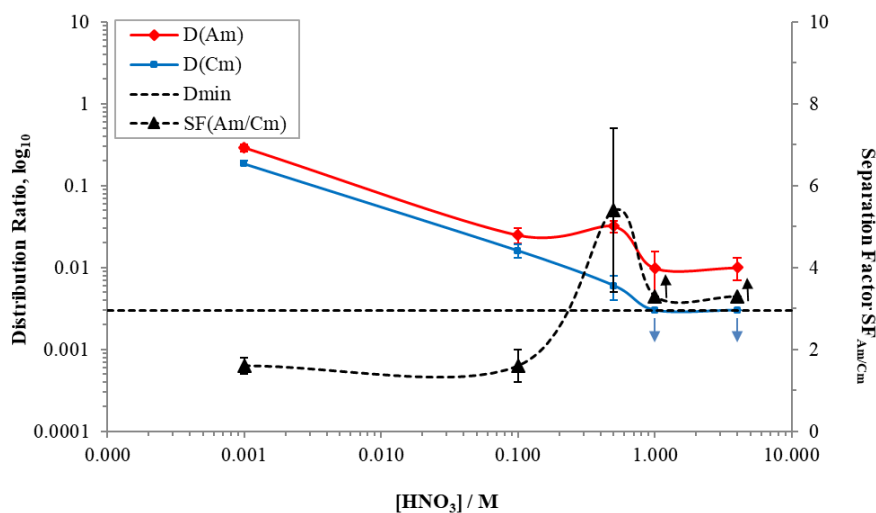


Figure 6 Extraction of Am(III) and Cm(III) by 5 mM tetra(4-hydroxyphenyl)-BTPhen **3** in octanol as a function of nitric acid concentration. The system was shaken for 90 mins at 1800 rpm.

Subsequently, the ligand was immobilized onto silica gel and the resulting functionalized silica gel **4** was used in a solid-liquid extraction system. Our previous work with this silica-immobilized extractant showed high weight distribution ratios across a range of nitric acid concentrations ($D_{\text{w,Am}} = 28 - 4883 \text{ mL g}^{-1}$, $D_{\text{w,Eu}} = 0.2 - 630 \text{ mL g}^{-1}$ from 0.001 – 4 M HNO_3) for Am(III) and Eu(III) and the highest separation factor value

was calculated to be $SF_{Am/Eu} \approx 140$ at 4 M HNO_3 .³² Herein, we report the effect of the concentration of perchloric acid on the extraction of Am(III), Eu(III), and Cm(III) (Figure 7) to test the effect of pH vs anion concentration on extraction selectivity because ClO_4^- is a non-chelating counterion, unlike the coordinating nitrate ion. When comparing these data, it can be seen that, similar to the nitric acid case reported previously,³² the separation factor $SF_{Am/Eu}$ initially increases with increasing $HClO_4$ concentration but then decreases sharply with perchloric acid concentrations higher than 0.1 M.

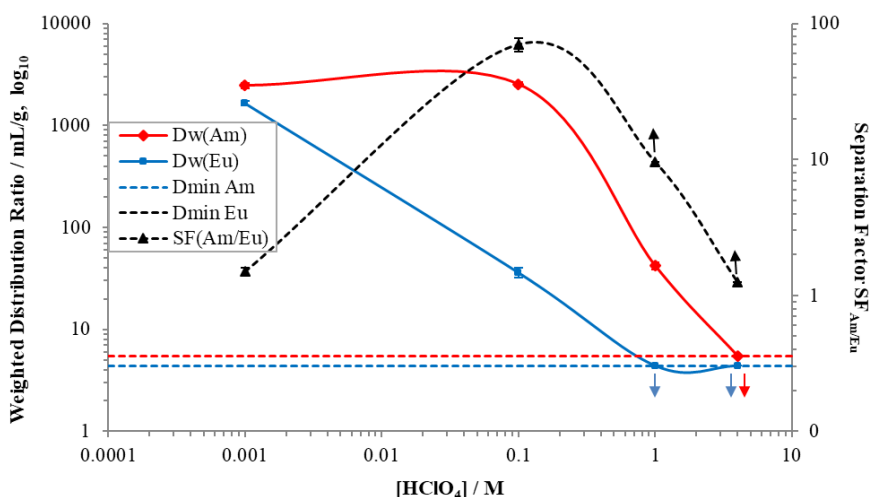


Figure 7 Extraction of Am(III) from Eu(III) by 6.4 mg of silica immobilized tetra(4-hydroxyphenyl)-BTPhen **4** as a function of perchloric acid concentration. $V/m = 143 \text{ mLg}^{-1}$. The system was shaken for 90 mins at 1800 rpm.

Therefore, upon comparing the extraction data, the immobilized tetra(4-hydroxyphenyl)-BTPhen **4** does not extract at higher concentrations of perchloric acid. However, the decrease of extraction efficiency with increasing acid concentration is much lower in nitric acid. Interestingly, the extraction data are not too dissimilar at lower concentrations of the acids. This would support the conclusion that pH is more important than the concentration of nitrate ions at $pH < 0.1$ M and the concentration of nitrate ions becomes more prevalent at concentrations > 0.1 M.

As previously reported, tetra-bromomethyl-BTBP on silica **5** demonstrated excellent extraction capacities for transition metals.³² Silica immobilized tetra(4-hydroxyphenyl)-BTPhen **4** was also tested for transition metal extraction. The immobilized ligand (1 g, ~9.8% BTPhen loading) was packed into a glass column (internal diameter = 13 mm), and washed with 2% HNO_3 solution (10 mL). Stock solutions (10 mL, 100 ppb) in 2% HNO_3 were passed through the column at rate of 1 mL per minute. The filtrate was collected and analysed by ICP-MS, indicating $>70\%$ uptake of Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Mo^{4+} , Ag^+ , Cd^{2+} , Pb^{2+} , Pd^{2+} ,

Os⁴⁺, Pt⁴⁺, Au³⁺, Zr⁴⁺, Nb⁵⁺, Hf⁴⁺, Ta⁵⁺, and W⁶⁺ at pH 0.5. Re⁴⁺, Ir³⁺ and Sb⁵⁺ showed lower uptakes at 68, 40, 50% respectively (Figure 8). More significantly, Ni²⁺, Pd²⁺, Ag⁺ and Cd³⁺, the corrosion and fission products from PUREX raffinates, were found to be near quantitatively extracted. Like its BTBP counterpart, the ligand did not extract Group I, II or III metals (Li⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺, Al³⁺).

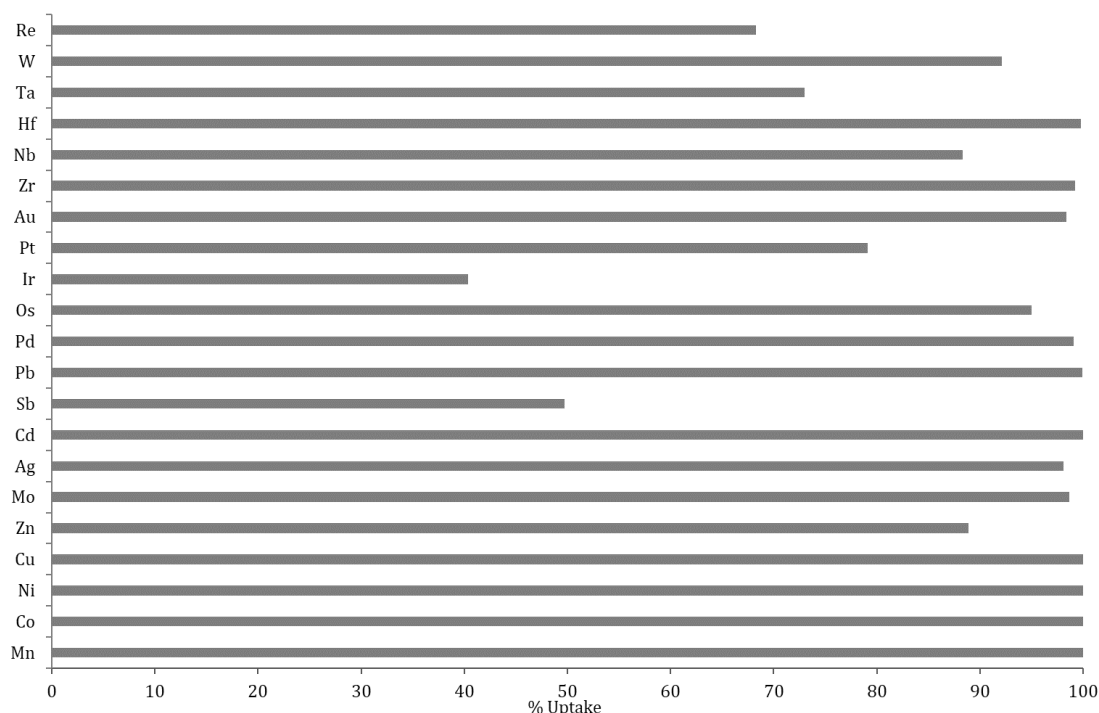


Figure 8 Percentage uptake of metal ions (10 ppb) from aqueous solution at pH 0.5 (HNO₃) by tetra(4-hydroxyphenyl)-BTPhen functionalized silica **4**

In conclusion, we report the effect of diluent on the liquid-liquid extraction properties of tetra(4-hydroxyphenyl)-BTPhen **3**. Cyclohexanone offers higher solubility and greater separation factors for actinide–lanthanide extraction over octanol; whereas, with octanol, the *D*-values were too low for practical application. The ligand **3** was also immobilized onto silica gel and the effects of a non-ligating acid (perchloric acid) versus a ligating acid (nitric acid) were examined. Extraction of both actinides and lanthanides was seen at lower concentrations of perchloric acid (up to 0.1 M HClO₄) but not at higher concentration as had previously been observed with nitric acid. These findings support the conclusion that the extraction ability of a ligand is strongly correlated with the complexation of the acid anions to the metal(III) ion and is only pH dependent at very low acid concentrations. The immobilized ligand system **4** was also tested for extraction of transition metals, showing >70% uptake of most with particular affinity for Ni²⁺, Pd²⁺, Ag⁺ and Cd²⁺, the corrosion and fission products from PUREX raffinates

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